Indian Journal of Chemistry
Vol. 36B, February 1997, pp. 185-186

Note

Reduction of nitroarenes to anilines with Zn-$AlCl_3.6H_2O$-THF-H_2O system

Papori Goswami & Pritish Chowdhury*
Organic Chemistry Division, Regional Research Laboratory,
Jorhat 785 006, India
Received 12 March 1996; revised 24 June 1996

Nitroarenes are conveniently reduced to their corresponding anilines by a system consisting of Zn-$AlCl_3.6H_2O$-THF-H_2O at room temperature in excellent yields.

Aluminium based reagents have been found to be useful in synthetic organic chemistry because of their low cost, easy availability and ease of handling and therefore are gaining importance for the last few years[1]. Recently, we have observed[2] that a system comprising zinc-aluminium chloride hexahydrate-tetrahydrofuran and water chemoselectively deoxygenate a carbonyl functions, specially cyclic ketones to give their methylene derivatives in good yields as well as reduces α, β-unsaturated carbonyl compounds to their α, β-unsaturated hydroxy derivatives in high yields. In this note, we report the reduction of aromatic nitro compounds to the corresponding amino derivatives using the above system at room temperature under mild reaction conditions. Thus, the nitroarenes (**1-10**) gave their corresponding anilines in excellent yields (80-90%) when treated with the above system at room temperature (Table I). Although, zinc mediated reductions of nitroarenes to anilines using Zn-$CaCl_2$, Zn-HCl, Zn-NH_4Cl, Zn-NaOH etc. are well known[3], but most of them exhibit severe drawbacks. For example, zinc in mineral acids like hydrochloric acid often produces chloronitro derivatives in a significant amount and also the method is not very suitable for the substrate containing acid sensitive labile functionalities. Another zinc mediated reduction of nitroarenes using Zn-NH_4Cl mainly gives highly toxic phenylhydroxylamines as major products. The other methods like Zn-$CaCl_2$-H_2O or Zn- NaOH etc. require drastic reaction conditions. Besides zinc mediated reduction of nitroarenes, several other methods have also been reported[4-9] in the literature using different reagents like $SnCl_2$, $NaBH_4$ and Pd/C catalyst etc. The high cost of the reagents, moderate yield of the desired arylamines, stringent reaction conditions etc. are the main drawbacks for many of these procedures. In view of these, the present system based on aluminium reagent using aluminium chloride-hexahydrate which is very cheap, non-toxic and therefore environmental friendly, would have much advantages over the existing zinc mediated as well as other methods for this reduction. Moreover, the present method also does not affect the double bond in an α, β - unsaturated carbonyl system unlike the other metal-salt system[9a], instead gives their simple reduced products. Thus, when nitrobenzene was treated with the present system based on aluminium reagent at room temperature in the presence of carvone **11**, aniline and carveol **12** were obtained in almost quantitative yield. The compound **12** on oxidation with activated MnO_2 or pyridinium chlorochromate gave back the compound **11**.

Therefore, it is believed that this selective, sim-

Table I—Reductions of nitroarenes (**1-10**) with Zn-$AlCl_3.6H_2O$-THF-H_2O system at room temperature

Nitroarenes	Products	Yield (%)	m.p./b.p. ± °C
Nitrobenzene (**1**)	Aniline	95	183
p-Chloronitrobenzene (**2**)	*p*-Chloroaniline	90	230
3-Nitrobenzoic acid (**3**)	3-Aminobenzoic acid	85	175
Methyl 4-nitrobenzoate (**4**)	Methyl 4-aminobenzoate	85	108
2-Nitrophenol (**5**)	2-Aminophenol	75	170
4-Nitrotoluene (**6**)	*p*-Toluidine	85	40
1-Nitronaphthalene (**7**)	1-Aminonaphthalene	80	44
2-Nitronapthalene (**8**)	2-Aminonaphthalene	80	110
1,3-Dinitrobenzene (**9**)	1,3-Phenylenediamine	80	62
5-Nitroindole (**10**)	5-Aminoindole	80	129

ple as well as mild and eco-friendly method may find application for the reduction of nitroarenes to anilines and therefore would be a useful addition to the existing methods. The difference in the redox potentials of Zn/Zn^{++} and Al/Al^{+++} system is high enough to effect immediate reduction of nitroarenes to their amino derivatives. Further work of this reagent system on steroidal nitro compounds and other functionalities to explore the reduction of α, β - unsaturated ketones in terms of the product alcohols formed and their optical purity are in progress.

Experimental

Melting points were determined on a Mettler FP 62 instrument and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237B spectrophotometer for solutions in chloroform; ^1H NMR spectra in $CDCl_3$ on Varian 60 MHz instrument and mass spectra on an INCOS 50 GC- MS instrument. TLC were performed on silica gel (E. Merck) and the plates were activated at 100°C for 1hr.

Reduction of nitroarenes to anilines: General procedure. The substrate (0.5 mmole) in THF (4 mL) was added to a mixture of Zn - dust and $lCl_3.6H_2O$ (500 mg; 1:6 mole/mole) containing a little water (2-3 drops), when a mild exothermic reaction with the evolution of H_2 gas was observed. The reaction mixture was kept at room temperature for 5 hr, filtered and the filtrate was poured into cold water (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The organic extract was then evaporated under reduced pressure to furnish a residue which on purification by preparative TLC gave the desired product. The products (cf. Table I) thus obtained were identified by direct comparison with authentic samples (TLC, IR, ^1H NMR, mass spectra and mixed melting points).

References

1 Chen J G, Beebe (Jr) T P, rowell J E & Yates (Jr) J T, *J Am Chem Soc*, 109, **1987**, 1726.
2 Chowdhury P K & Borah Parinita, *J Chem Res (S)*, **1994**, 230.
3 (a) Larock R C, *in Comprehensive Organic Transformations*, (VCH Publications, New York), **1989**.
(b) Hudlicky M, *in Reductions in Organic Chemistry*, (Ellis Horwood Ltd, Chichester), **1984**.
4 Oelschlager.H, *Chem Ber*, 89, **1956**, 2025.
5 Cortese N A & Heck R F, *J Org Chem*, 42, **1977**, 3491.
6 Alper H & Gopal M, *J Chem Soc Chem Commun*, **1980**, 821.
7 Alper H & Amaratunga S, *Tetrahedron Lett*, 21, **1980**, 2608.
8 Hane B H & Jang D G, *Tetrahedron Lett*, 31, **1990**, 1181.
9 (a) Sarmah P & Baruah N C, *Tetrahedron Lett*, 31, **1990**, 4065.
(b) Baruah R N, *Indian J Chem*, 33, **1994**, 758.